

AN IMPROVED TECHNIQUE FOR THE
HYDRODESULFURIZATION OF COAL CHARs

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INTRODUCTION

The sulfur content of many coals is too high to comply with the EPA standard for power plant fuels. The current alternatives for utilizing coal as a fuel include either complete gasification of the coal with the sulfur removal effected by conventional gas treatment, or direct combustion of the coal with stack gas scrubbing.

In a carbonization process such as the patented GR&D flash pyrolysis process, the coal is converted into char. Although the sulfur content of the chars is normally less than that of the parent coals, most chars must still be treated to reduce the sulfur content to comply with EPA standards. We have developed an improved hydrodesulfurization process that accomplishes the required sulfur reduction. We propose that this process is more advantageous than the current alternatives for utilizing the coal directly.

Earlier work conducted by Consolidation Coal Company (1, 2) and by FMC Corporation (3, 4) demonstrated that hydrogen treatment of the char at elevated temperatures is effective in the removal of sulfur. However, the presence of the hydrogen sulfide product gas strongly inhibited the removal of additional sulfur. Either a large excess flow of hydrogen had to be maintained or the introduction of a hydrogen sulfide acceptor such as dolomite was necessary (3,4, 5). However, the utilization of an acceptor presents several difficult problems which include separation from the char, regeneration, and loss of acceptor activity. Obviously, the direct treatment of the char with hydrogen to remove sulfur would be more practical if the effects of the hydrogen sulfide inhibition could be reduced. Our work shows that the effect of the hydrogen sulfide inhibition can be minimized by pretreating the char with acid. Hydrogen sulfide inhibition isotherms (char sulfur contents at extended residence times) indicated that a significantly greater concentration of hydrogen sulfide is allowable for the acid-treated chars than for the untreated chars. This represents a significant reduction in both the capital and operating costs of a commercial hydrodesulfurization facility by

allowing a reduction in the hydrogen throughput. For a counter-current hydrosulfurization system with three stages, the hydrogen requirement for acid-treated char is only 12% of that for the untreated char.

EXPERIMENTAL

Apparatus

The experimental apparatus utilized in the hydrogen treatment of the char (Figure 1) consists of a 4' x 19mm I-D quartz reactor which is inserted in a Hevi Duty electric furnace. The ends of the reactor are sealed with Teflon gaskets and are cooled by water circulating through copper coils. The gas flow to the reactor is controlled by means of a rotameter, and the system pressure is maintained by a back-pressure regulator. Gas flow calibrations were obtained with a wet-test meter.

The reactor was packed with ceramic burl saddles up to the middle of the hot zone, and a Kaowool plug was positioned on top of the saddles to prevent char from falling through the reactor. In addition, a Kaowool plug was positioned at the top of the hot zone to prevent elutriation of the char particles.

Procedure

Helium gas flow at the reaction pressure was maintained during reactor start-up. The temperature was established by an Alnor controller in conjunction with a chromel-alumel thermocouple positioned externally to the reactor. After sufficient saturation time was allowed at the desired temperature, hydrogen or a mixture of hydrogen and hydrogen sulfide from calibrated cylinders was introduced to the reactor for the desired reaction time. The system was then purged with helium, and the temperature was allowed to return to ambient.

Char Preparation

Chars were prepared by carbonizing several selected coals under nitrogen at elevated temperatures. These coals included a high volatile C bituminous coal from West Kentucky and a high sulfur bituminous coal from Illinois. Chars were produced both from run-of-mine coals and from samples which had been physically beneficiated by a sink/float technique prior to the carbonization. The chars

were ground and screened to the desired particle size. The chars to be acid-treated were leached with 80°C hydrochloric acid for approximately five minutes. After the acid leach, the char was washed with water until the water was free of chloride ion as determined by the silver nitrate test.

Chemical Analyses

A complete sulfur analysis was performed on the reactant and product chars. The total char sulfur was measured by the Eschka method. The sulfide, sulfate, and pyritic sulfur forms were also measured. An ultimate analysis was also performed to allow estimation of the char combustion heats.

The metals in the char ash were analyzed by either emission spectra or by atomic absorption. Fe^{+2} was measured by leaching the char with a solution of HF and H_2SO_4 followed by titration with KMnO_4 . Fe^0 was measured by reacting the char with a solution of Hg_2Cl_2 followed by atomic absorption of the final solution. Very little Fe^0 was observed in any of the tests. Fe^{+3} was determined by difference.

DISCUSSION

Previous work has demonstrated that the presence of hydrogen sulfide greatly inhibits the hydrodesulfurization of char. In addition, inhibition isotherms were presented that show plateaus of sulfur in the char at low concentrations of hydrogen sulfide in the treatment gas. (2, 6) These plateaus were attributed to the equilibrium in the reduction of iron sulfide.



The presence of calcium sulfide, which is irreducible by hydrogen treatment, was also noted.

Although the reaction of carbonaceous materials with hydrogen and hydrogen sulfide mixtures is reversible, the reaction is not a true equilibrium process (2). The type of carbonaceous material, the type of pretreatment, and the temperature and time of treatment all affect the extent of the reaction. Since both inorganic and organic sulfur forms exist in the char, different methods must be employed to completely remove both forms. We chose to study the effects of an acid pretreatment to remove inorganic sulfur and a subsequent hydrogen treatment to remove the organic sulfur. However, the additional removal of the iron and calcium hydrodesulfurization reaction.

Hydrogen Sulfide Inhibition Isotherms

The hydrogen sulfide inhibition isotherms at 1600°F and 50 psig for three chars prepared from West Kentucky Coal are shown in Figure 2. The three char samples were prepared by carbonizing the run-of-mine coal, floating the coal in a 1.55 s.g. ZnCl_2 solution prior to carbonization, and by acid treating the char from the floated coal. The chars were ground and screened to a -80 +270 mesh particle size. The char samples were then hydrogen treated for approximately 2-1/2 hours. The char from the run-of-mine coal exhibited the greatest hydrogen sulfide inhibition. Although the char from the floated coal compares favorably with the acid-treated char in the limit of pure hydrogen, the acid-treated char exhibited the least hydrogen sulfide inhibition.

Hydrogen sulfide inhibition isotherms for three similar chars prepared from the Illinois coal are compared with the isotherms for the West Kentucky coal chars in Figure 3. Although the hydrogen sulfide inhibition is in general slightly less severe for the Illinois coal chars, the floating and acid treating operations also reduce the severity of the hydrogen sulfide inhibition for these chars. However, the inhibition isotherms for the acid-treated chars from the West Kentucky and Illinois coals are practically identical.

The effect of the iron and calcium content of the chars on the inhibition isotherms is apparent in Table I. The quantity of iron and calcium is highest in both the West Kentucky and Illinois run-of-mine chars. The higher iron content of the West Kentucky char may be responsible for the slightly more severe inhibition isotherms shown in Figure 2. An intermediate quantity of iron and calcium is contained in the two chars from the floated coals. The higher iron content of the West Kentucky char again corresponds to a slightly more severe inhibition isotherm. The lowest quantity of iron and calcium is contained in the acid-treated chars. These chars also have the least severe inhibition isotherms.

Acid Treatment

Hydrochloric acid was utilized in the preparation of the acid-treated chars in Table I. Although significant quantities of ash were removed by floating the coal, the char from the floated coal still contained appreciable quantities of iron and calcium. The final reduction in the quantities of iron and calcium was accomplished by the acid treatment. The char ash also contains large quantities of silicon, aluminum, potassium, and sodium, but these were only slightly affected by the acid treatment.

Some sulfur reduction is also accomplished in the physical beneficiation step by the removal of pyrite. Almost all of the remaining pyrite sulfur is converted to FeS during carbonization. This sulfur is removed by the acid treatment along with additional quantities of Fe^{+2} , Fe^{+3} , and calcium. The total sulfur in the char of the beneficiated West Kentucky coal is reduced from 1.90 to 1.34% by the acid treatment, which is in very close agreement with the measured reduction in sulfide sulfur from 0.57 to 0.10%.

The type of mineral acid utilized in the acid treatment does not appear to affect the final desulfurization. The inhibition isotherms for sulfuric acid-treated char were identical to those chars treated with hydrochloric acid (Figure 2).

Finally, the beneficiation operation is not essential to the final desulfurization. The inhibition isotherms for acid-treated chars from the run-of-mine coals were identical to those chars which were prepared from floated coals. The advantage of the beneficiation operation appears to be in the initial removal of most of the pyritic sulfur and in a reduction of the quantity of acid consumed in the char treatment.

Optimum Desulfurization Temperatures

Chars prepared at low temperatures and short residence times might be expected to have a more labile form of organic sulfur than chars prepared at high temperatures and long residence times. The more severe conditions would increase the probability of thermally fixing the organic sulfur, which would be stable in the presence of hydrogen (7). Since the chars in this study were prepared by carbonization of the coal at the anticipated desulfurization temperature for over two hours, any expected thermal fixing of char sulfur should have occurred.

The optimum desulfurization temperature for the chars from the West Kentucky coal was found to be between 1700 and 1800°F as illustrated in Figure 4. This same optimum temperature occurred for all coal and char pretreatment methods.

Much lower optimum desulfurization temperatures of 1300 and 1470°F had been found in the desulfurization of petroleum coke with hydrogen (8) and butagas, a coke-oven gas which is predominately butane (9). The latter optimum was attributed to the sintering of the coke particle with a subsequent loss of available surface area.

However, no evidence of sintering was observed in the case of the coal chars.

Hydrodesulfurization Kinetics

Although most of the screening of variables has been accomplished in terms of the hydrogen sulfide inhibition isotherm, the hydrodesulfurization of char is not a true equilibrium process. An adequate description of the kinetics of hydrodesulfurization is essential if the design of commercial equipment is anticipated. We are currently undertaking such a kinetic study.

The kinetic data for the hydrodesulfurization of floated char and acid-treated char from the West Kentucky coal at 1700°F and 50 psig is shown in Figure 5. These chars were ground to a -200 mesh particle size. Rate data are shown for various compositions of hydrogen and hydrogen sulfide reactant.

Although the initial sulfur content of the acid-treated char is lower than that for the floated char, the initial disappearance rates of sulfur for the two chars in contact with pure hydrogen are quite similar. In contrast, the disappearance rate of sulfur for the acid-treated char in contact with even a small quantity of hydrogen sulfide is faster than that for the floated char. In addition, these data at long residence times indicate much lower final sulfur contents for the acid-treated chars.

The mechanism of hydrodesulfurization appears to be quite complex. For example, the removal of the first fifty percent of the sulfur in the acid-treated char can be described by first order kinetics while the remainder appears to follow a zero order reaction. These data cannot be explained by a hydrogen sulfide reverse reaction. If the flow rate of hydrogen were maintained sufficiently low, the sulfur released by the hydrodesulfurization might become more firmly attached to the char. However, tests conducted at one-half the normal experimental hydrogen flow demonstrated that the effect of a reverse reaction was not important in this study. The results of these tests are indicated in Table II.

The hydrodesulfurization kinetics might be explained by a rapid evolution of sulfur on the char surface followed by the slower removal of sulfur in the char interior. Since similar rates were

obtained from tests conducted at 1600 and 1700°F, the hydrodesulfurization kinetics is probably not controlled by a chemical reaction mechanism. Also, tests conducted on a -60 +80 mesh char were not appreciably different from similar tests conducted on the same char which was ground to a -200 mesh particle size. These data are in accordance with a pore diffusion mechanism (3).

Counter-current Hydrodesulfurization

A significant reduction in the hydrogen requirement of any commercial hydrodesulfurization process can be realized by counter-current staging. However large throughputs of hydrogen are still required if untreated char is to comply with EPA standards. In contrast, the acid-treated chars can be handled quite effectively by the counter-current process.

Based on calculated heats of combustion of 12,000 and 13,000 Btu/lb char for floated char and acid-treated char and the EPA standard for 1.2 lb SO₂/MM Btu (10), final char sulfur contents of 0.72 and 0.78% would meet the criterion for the West Kentucky coal. If the floated char were to be desulfurized in a single stage, 73 pounds of hydrogen would be required for every 100 pounds of char. If the floated char were to be desulfurized in three counter-current stages, the hydrogen requirement would be reduced to 8.5 pounds. However, only 1.0 pounds of hydrogen is required to desulfurize 100 pounds of acid-treated char in three counter-current stages. In the multistage process, the hydrogen requirement for acid-treated char is only 12% as high as that for floated char.

Conclusions

The effectiveness of the hydrodesulfurization process for coal chars is significantly improved, in turn, by the physical beneficiation of the parent coal and by the acid treatment of the product char. These processes have been effective in the removal of iron and calcium constituents which appear to contribute to the severity of the hydrogen sulfide inhibition. The acid treatment is particularly advantageous in that both the iron and calcium contents of the char are reduced well below that of the floated coal char. In addition, the remaining ash constituents which are not removed by the coal beneficiation treatment are not affected by the acid treatment. Thus, the consumption of the acid is minimized.

A significant reduction in the hydrogen requirement of the commercial hydrodesulfurization process can be realized by counter-

current staging. An additional significant reduction is accomplished by acid treatment of the char. In the multistage process, the hydrogen treatment for acid-treated char from the West Kentucky coal is only 12% of that required for the untreated char from the beneficiated coal.

The optimum desulfurization temperature which was determined for the chars of the West Kentucky coal used in this study appears to be in the range of 1700 to 1800°F. However, this optimum temperature may vary with the method of char preparation.

Preliminary kinetics studies indicate that the acid treatment technique reduces the effect of hydrogen sulfide inhibition in the disappearance of the char sulfur.

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Table IChar Analysis for Ash, Calcium, and Iron

<u>Char</u>	<u>Ash</u> <u>Wt. %</u>	<u>Ca</u> <u>Wt. %</u>	<u>Fe</u> <u>Wt. %</u>	<u>Fe⁺²</u> <u>Wt. %</u>	<u>Fe⁺³</u> <u>Wt. %</u>
West Kentucky Run-of-Mine Carbonized at 1600°F	23.0	0.9	2.8	1.3	1.5
West Kentucky 1.55 S.G. Float Carbonized at 1600°F	10.9	0.1	1.13	0.67	0.46
West Kentucky 1.55 S.G. Float Carbonized at 1600°F and acid-treated	9.5	0.06	0.32	0.03	0.29
Illinois Run-of-Mine Carbonized at 1600°F	16.06	1.01	1.75	1.35	0.40
Illinois 1.55 S.G. Float Carbonized at 1600°F	9.93	0.13	0.76	0.37	0.39
Illinois 1.55 S.G. Float Carbonized at 1600°F and acid-treated	9.33	0.08	0.27	0.005	0.27

Table IIEffect of Hydrogen Flow Rate on Desulfurization ofAcid-Treated Char from West Kentucky Coal at1700°F and 50 psig

<u>Flow Rate</u> <u>SCFM</u>	<u>Time</u> <u>Min.</u>	<u>Char Sulfur</u> <u>Wt %</u>	<u>Superficial Velocity</u> <u>ft/sec</u>
0.030	5	0.92	0.151
0.015	5	0.90	0.076
0.030	15	0.79	0.151
0.015	15	0.77	0.076

FIGURE 1
EXPERIMENTAL APPARATUS

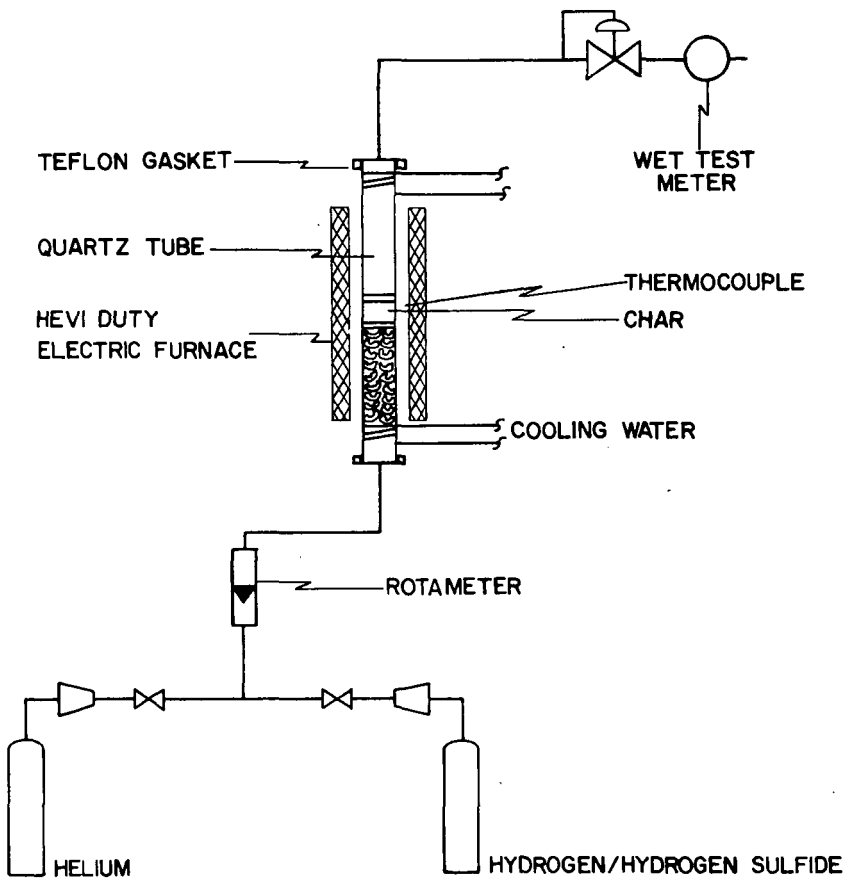


FIGURE 2
HYDROGEN SULFIDE INHIBITION ISOTHERM FOR WEST KENTUCKY
COAL CHAR

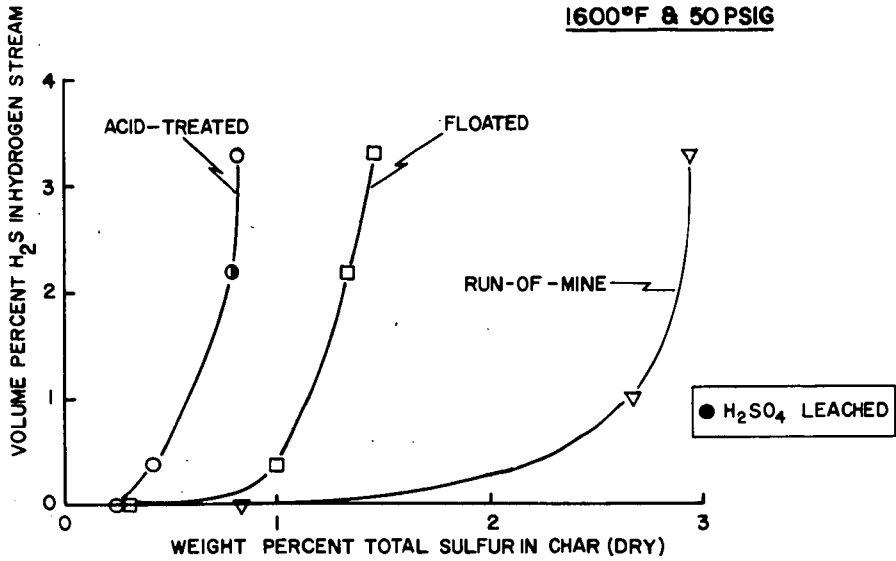


FIGURE 3
COMPARISON OF WEST KENTUCKY AND ILLINOIS COAL CHARS

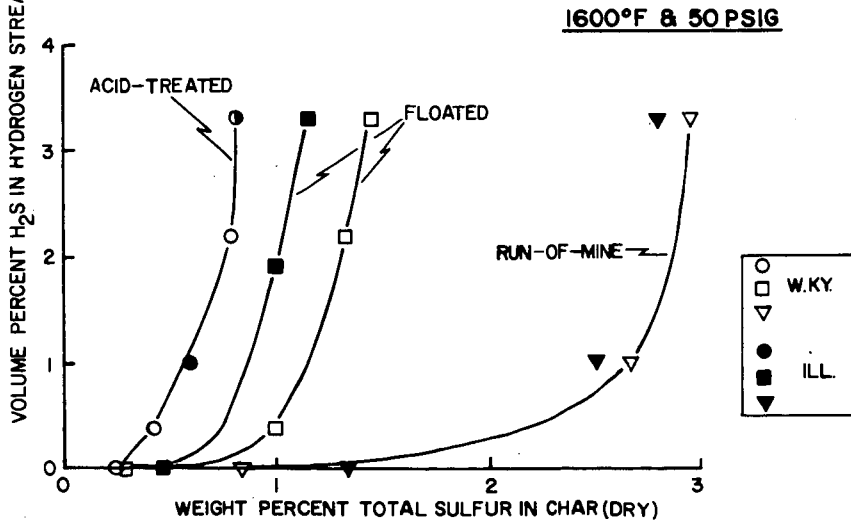


FIGURE 4

VARIATION OF CHAR SULFUR WITH TEMPERATURE FOR WEST KENTUCKY COAL CHAR

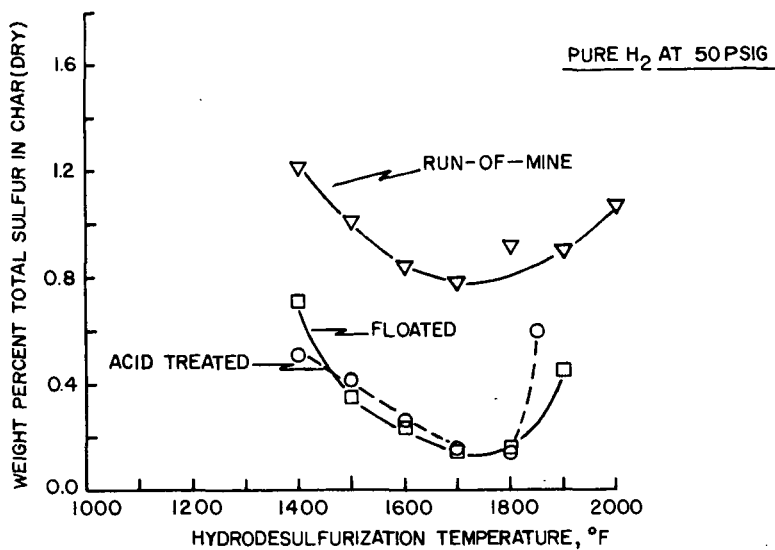


FIGURE 5
HYDRODESULFURIZATION KINETICS
OF WEST KENTUCKY COAL CHAR

